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A Comparative Study for the Removal of Methylene Blue Dye from Aqueous Solution by Novel Activated Carbon Based Adsorbents

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ABSTRACT

This study was conducted to assess the ability of the studied adsorbent, i.e. raw oak fruit hulls and the activated carbon prepared from oak fruit hull for removing the Methylene blue (MB) from aqueous solution. This study was conducted under various effective parameters, e.g., contact time, pH, MB concentration, adsorbent concentration. The optimum amount of each parameter was determined and the isotherm and kinetic studies were also carried out. The results revealed that the best results for MB removal efficiency are observed using the activated carbon prepared from oak fruit hulls. It was also observed that increasing the contact time, pH and adsorbent concentration provides better condition to enhance the dye removal efficiency and increasing the MB, hence reducing the removal efficiency. Furthermore, the results also clarified that the best models to describe the MB adsorption onto the raw oak fruit hulls and activated carbon are the Langmuir model 1 (R^2=0.9971) and Langmuir 2 (R^2=0.7631), respectively. In addition, the adsorption of MB onto the raw oak fruit hulls and activated carbon are better fitted to pseudo-second-order model and zero-order model, respectively. Finally, it can be concluded that the activated carbon prepared from the raw oak fruit hulls is more valuble than the raw oak fruit hull for removing the MB. Prog. Color Colorants Coat. 12 (2019), 133-144© Institute for Color Science and Technology.

1. Introduction

The colorful wastewaters released from various industries such as textiles, leather, paper, printing, cosmetics, etc. are considered as one of the important challenges for the communities due to the toxicity and carcinogenicity of the applied dyes [1-3]. Textile industries are accounted for the greatest industries to use the dyes and to generate the colorful wastewater [4-6]. The presence of aromatic rings in the structure of dyes lead to the increase of their resistance against the biological degradation [7-9]. Methylene Blue (MB), a cationic azo dye, is broadly applied in chemistry, biology, medical science and dyeing industry [10, 11]. Despite this, this dye has been found to be toxic and

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have different detrimental effects, as follows: Eye burn, skin irritation, breathing problems, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia, convulsions, tachycardia, etc. [12-14]. These mentioned subjects reveal the importance of removing dyes, e.g. methylene blue, from aqueous wastewaters to avoid destroying the life cycle.

Literature reviews have been indicative of application of various techniques, e.g., adsorption, biosorption, coagulation/flocculation, advanced oxidation, ozonation and membrane filtration for dye removal [15-17]. Adsorption technique has been known as a favorable and successful method for elimination of dyes due to its advantages such as low cost, ease of design and application, etc., [18-20]. The frequently used adsorbent is the activated carbon that has gained a great reputation in removal of dyes because of its noteworthy efficiency; nevertheless, due to its expensiveness, this can not be a suitable option in developing countries and the generation of a novel affordable adsorbent has always been considered as the research priorities for scientists [21-24]. This has been led to the evaluation and examination of various materials such as activated coconut shell [25-26, maize silk powder [27-28], activated carbon prepared from karanj fruit hulls [29], activated carbon obtained from Ficuscaricabast [10], Aleppo pine cones [30-32], etc. The results obtained from the use of these materials were indicative of a bright future to find suitable alternatives.

In this study, the potential of raw oak fruit hull and activated carbon derived from it for removing Methylene Blue from aqueous solution was assessed and compared. This study was conducted using different operational parameters including contact time, pH, adsorbent concentration, initial concentration of the studied dye to obtain theie optimum values.

2. Materials and Methods

2.1. Materials

Methylene Blue (MB, Chemical formula: $C_{16}H_{18}N_3$, Molecular weight: 319.85 g/mol), HCl and NaOH were purchased from Merck CO., Germany. Distilled water was used in all steps of the study. The stock solution of the dye was prepared by dissolving 1 g in 1000 mL of distilled water and the required concentration of the dye was prepared using the stock solution. The regulation solution pH was carried out using 0.1 N HCl and NaOH.

2.2. Preparation of activated carbon from raw oak fruit hull

Oak fruit was provided from forests of Lorestan province, Iran. After separating the oak hulls, they were initially washed with distilled water several times to eliminate surface contaminations and dust. Afterward, they were placed in oven at 105 °C for 3 hours. After drying, the samples were crushed and sieved using 100 mesh sieve. Consequently, they were again washed several times with distilled water and re-dried. The resultant raw adsorbent was kept in the desiccator.

After collecting the Oak fruits, their hulls were separated and were washed with water and dried in oven at 105 °C for 60 min. Then, they were crushed into 2-3 mm particles and heated in quartz furnace at 450 °C and 750 °C for 120 and 30 min, respectively. The obtained particles were washed by distilled water and dried in oven at 105 °C for 60 min. the obtained activated carbon was stored to utilize in the experiments. It should be noted that, in order to providethe vacuum situation in the furnace, N_2 gas was used.

2.3. Characterization of the adsorbents

The characteristics of the prepared adsorbents were studied using SEM and FT-IR techniques. Scanning electronic microscopic (SEM) (Jeol MODEL Jsm-T330) was used to study the surface morphology of the adsorbent. Functional groups of the adsorbent's surface were determined by Fourier transform infrared (FT-IR) (Perkin Elmer of spectrum one model) in the wavelength range of 450-4000 cm^{-1}.

2.4. Experimental procedure

In the present study, the dye removal efficiency of the adsorbents was assessed in a batch system using a 500 mL Erlenmeyer flask Meyer. The effect of parameters, i.e. pH, adsorbent concentration, reaction time, dye concentration, and temperature was evaluated. In each step, 250 mL of the dye with certain concentration with a specific adsorbents concentration were added to the flask and mixed at 140 rpm for a predetermined time. The obtained samples were left for 30 min and then they were analyzed using UV-visible spectrophotometer (DR-5000) at λ_{max}=636 nm. Finally, the adsorption efficiency and adsorption capacity were calculated using the following equations:

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q = \frac{(C_0 - C_e)V}{M} \quad (2)$$

where C_0 and C_e are the initial and final concentrations of the MB in the solution, respectively, V (L) is the solution volume, M is the adsorbent mass (g).

2.5. Isotherm studies

Analyzing the isotherm data is important for developing an equation that can be used to design it. In addition, the absorption isotherm can be used to describe the quality of the reactions between the adsorbent and the adsorbate and also to optimize the amount of the adsorbent. These studies were conducted using the models mentioned in Table 1.

2.6. Kinetic studies

The kinetics of adsorption provides valuable and constructive information about the rate of the adsorption process and probable rate controlling step. For this purpose, different kinetic models listed in Table 2 were utilized.

3. Results and Discussion

3.1. Characterization of the adsorbents

Figure 1 (a and b) shows the SEM images of the adsorbents, i.e. raw oak fruit hull and activated carbon derived from it. The studies of adsorbent morphology showed that activated carbon has very fine porosity and this porosity can be attributed to the presence of cellulosic material in the adsorbent structure. The materials that have lignin in their structure have a large porosity [34]. Various studies show that increasing the porosity of the adsorbent increases the contact surface and the adsorption of dye ions onto the adsorbent. So, porosity plays significant role in adsorption capability [35].

Table 1: Equations of adsorption isotherm models [33] .

Isotherm model	Main model	Linear model
Freundlich	$q_e = K_F ln(C_e)^{1/n}$	$lnq_t = lnK_F + n^{-1} inC_e$
Langmuir 1	$q_e = (q_m k_l C_e)/(1 + k_l C_e)$	type$(I) C_e/q_e = (1/\mathrm{k}_1 q_m) + (C_e/q_m)$
Langmuir 2		type(II)$1/q_e = (1/\mathrm{k}_1 q_m C_e) + (1/q_m)$
Langmuir 3		type(III)$q_e = q_m - (1/\mathrm{k_L}) q_e/C_e$
Langmuir 4		type(IV)$q_e/C_e = \mathrm{k_l} q_m - \mathrm{k_l} q_e$
Temkin	$q_e = q_m ln(k_t C_e)$	$q_e = q_m ln\ \mathrm{k_T} + q_m lnC_e$
Dubinin-Radushkevich	$q_e = q_m exp(-D_\varepsilon^2)$ $\varepsilon = RTln(1 + c_e^{-1})$	$ln\ \mathrm{q_e} = q_m - D\varepsilon^2$

Table 2: Equations of kinetic models [33].

Kinetic model	Main model	Linear model
Elovich	$q_t = \beta ln(\alpha\beta t)$	$q_t = \beta ln(\alpha\beta) + \beta lnt$
Zero order	$q_t = q_e = k_0 t$	$q_t = q_e - k_0 t$
First order	$q_e = q_t \exp(\mathrm{k_1 t})$	$\ln(q_e/q_t) = \mathrm{k_1 t}$
Second order	$q_t = \mathrm{q_e}/(1 + \mathrm{q_e k_2 t})$	$q_t^{-1} = q_e^{-1} + \mathrm{k_t t}$
Pseudo-first order	$q_t = q_e[1 - exp(\mathrm{k_{1p} t})]$	$ln(q_e - q_t) = lnq_e - \mathrm{k_{1p} t}$
Pseudo-second order	$q_t = \mathrm{k_{2p}} q_e^2 t/(1 + q_e \mathrm{k_{2p}} t)$	$q_t = \mathrm{k_{2p}} q_e^2 t/(1 + q_e \mathrm{k_{2p}} t)$
Intraparticle diffusion	$q_t = \mathrm{k_p} t^{0.5}$	-

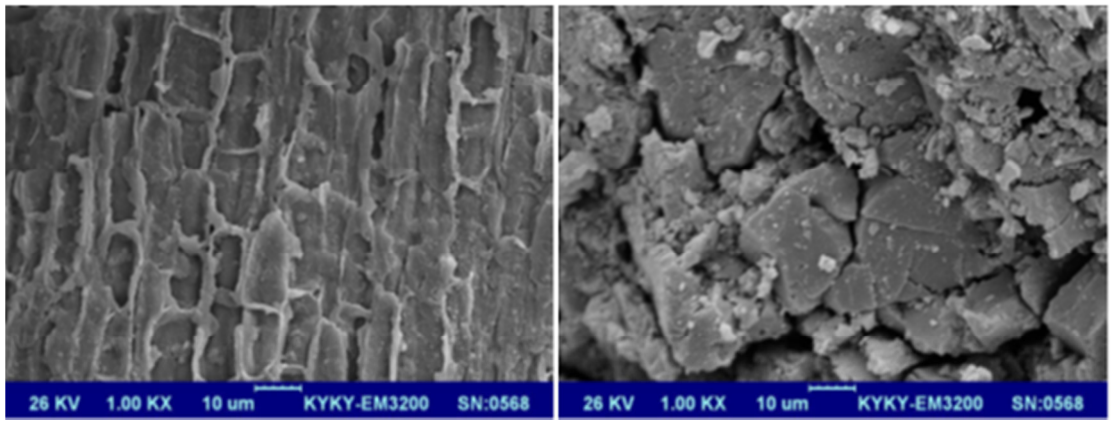

Figure1: SEM images of the adsorbents: (a) raw oak fruit hull and (b) activated carbon prepared from oak fruit hull.

Morphological studies also showed that the porosity of raw oak is less than the activated carbon. Figure 2 reveals the FT-IR spectra of the activated carbon prepared from the oak fruit hull. The specified peaks including the bands at 3379.22, 2921.19, 1616.42, 1733.94, 1517.05, 1448.21, 1035.15 and 1173 cm^{-1} which are related to stretching vibration of hydroxyl (OH) functional group at the adsorbent surface, the symmetric stretching frequency of the $-CH_3$ group, the stretching frequency of C = O in the carboxylic acid bonded to the inter molecular Hydrogen, the aromatic chains present on the adsorbent surface, the symmetric curve of $-CH_3$, the frequency variation in OH and the stretching frequency in the C-O-C in the cellulosic structure of the adsorbent, respectively [36, 37].

3.2. The effect of contact time on MB adsorption

The contact time has been introduced as an effective parameter in dye adsorption processes. The effect of this parameters under the studied conditions is represented in Figure 3 (a and b). As it can be seen from the figure, the MB removal efficiency using both adsorbents increases with contact time. However, the MB removal efficiency using the activated carbon prepared from oak fruit hull was higher (91% for MB concentration of 100 mg/L) than that of raw oak fruit hulls (15% for the concentration of 25 mg/L). The MB dye removal rapidly occurred at the initial times may be due to the greater accessibility to adsorption sites at the adsorbent surface [38].

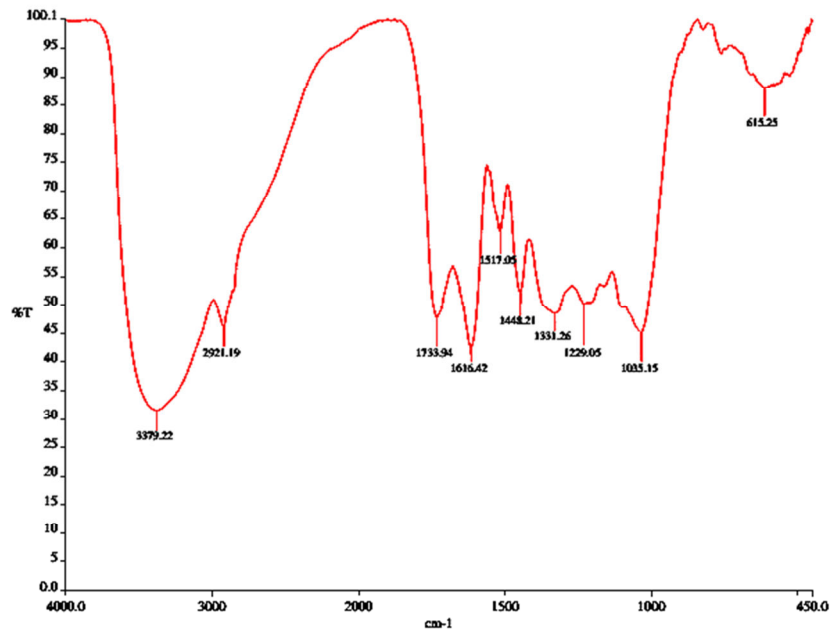

Figure 2: FT-IR spectra of the Activated carbon prepared from the oak fruit hull.

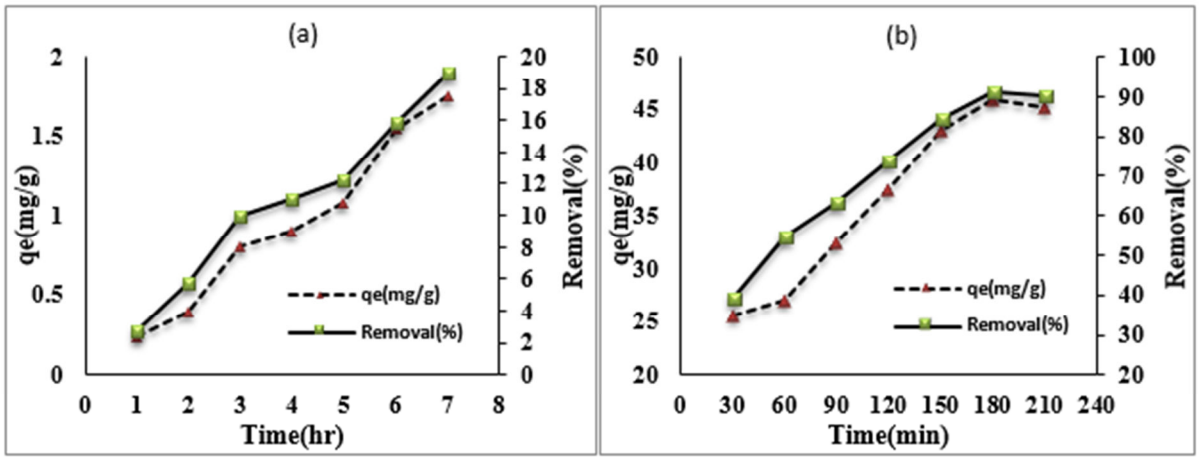

Figure 3: The effect of contact time on MB removal efficiency using: a) raw oak fruit hulls (pH=4, adsorbent concentration= 2g/L, MB concentration=25 mg/L, temperature=25 °C) and b) activated carbon (pH=6, adsorbent concentration= 2g/L, MB concentration=100 mg/L, temperature=25 °C).

It is also observed that the MB dye removal efficiency using the activated carbon and raw oak fruit hulls reaches the equilibrium after 180 and 360 min, respectively. Hameed et al. conducted a study to evaluate Methylene Blue onto adsorption efficiency onto the bamboo-based activated carbon. They observed that the dye adsorption efficiency onto activated carbon increases with time. They also found that the equilibrium time is observed after long time which it is consistent with the results of this study. They suggested that this phenomenon may be due to the three-step adsorption of MB onto the activated carbon, i.e. film diffusion, movement of solute from particle surface into interior site by pore diffusion and finally, adsorption into active sites at the interior of the adsorbent particle [39, 40].

3.3. Effect of pH on MB adsorption efficiency

In the adsorption process, the pH of the solution is one of the important factors affecting the dye structure and adsorption surface, ionization degree and removal efficiency[41]. In present study, the effect of the pH was studied at different pH values (2, 4, 6, 8, and 10). This study was performed using 25 mg/L of MB for raw oak hulls and 100 mg/L for activated carbon, 2 mg/L of adsorbent concentration and contact time of 180 and 360 min. According to Figure 4, the dye removal efficiency increases by pH value. This can be attributed to the cationic structure of MB and the point of zero charge. The pH-pzc is an imperative factor that illustrates the type of surface active centers and the adsorption ability of the surface. It has also been reported that the better cationic dye removal efficiency is obtained at $pH>pH_{pzc}$ because the adsorbent surface is negatively charged in these pH values [42]. Since the pH_{pzc} of the raw oak fruit hulls and the prepared activated carbon are 3.5 and 4, respectively, the MB adsorption onto these adsorbents should occur at pH values greater than 3.5 and 4 due to the formation of electrostatic attraction between negatively charged surface of the adsorbent and positively charged MB dye. These results are also confirmed by the results reported by Novais et al. and Regti et al. [10, 43].

3.4. Effect of MB dye concentration on adsorption efficiency

Figure 5 shows the results obtained for the effect of MB concentration on the adsorbents. This was carried out using MB concentration in the range of 25-150 mg/L. As can be seen in Figure 5, increasing the MB dye concentration led to decrease the removal efficiency for both adsorbents; increasing the MB dye concentration from 25 to 200 mg/L increased the removal efficiency from 87 to 80% using the prepared activated carbon and from 15 to 1.5% using the raw oak fruit hulls. The reason is that the adsorbents have limited adsorption sites and, by increasing the concentration of MB, they are rapidly saturated and the removal efficiency is reduced. This is consistent with the results of previous studies [21, 44].

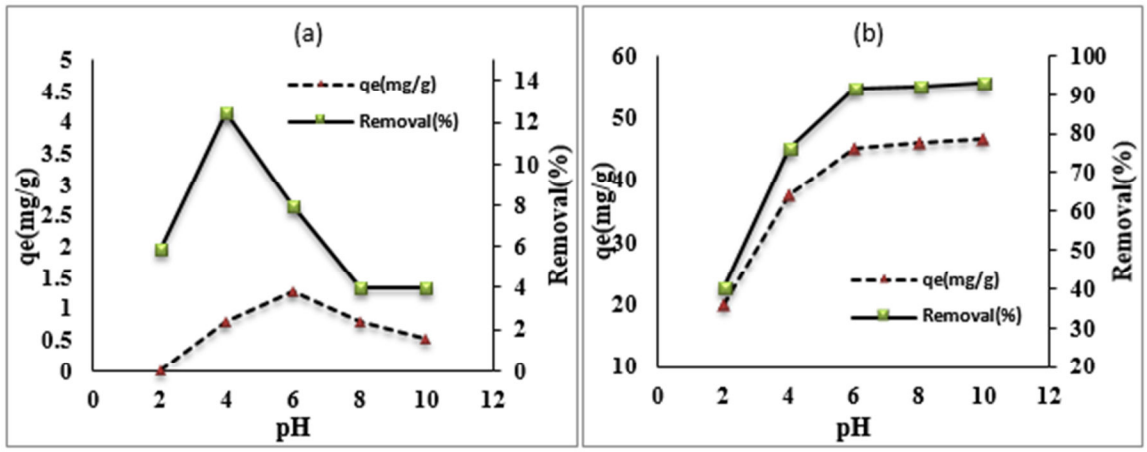

Figure 4: The effect of pH on MB removal efficiency using: a) raw oak fruit hulls (contact time=360 min, adsorbent concentration= 2g/L, MB concentration=25 mg/L, temperature=25 °C) and b) activated carbon (contact time=6, adsorbent concentration= 2g/L, MB concentration=100 mg/L, temperature=25 °C).

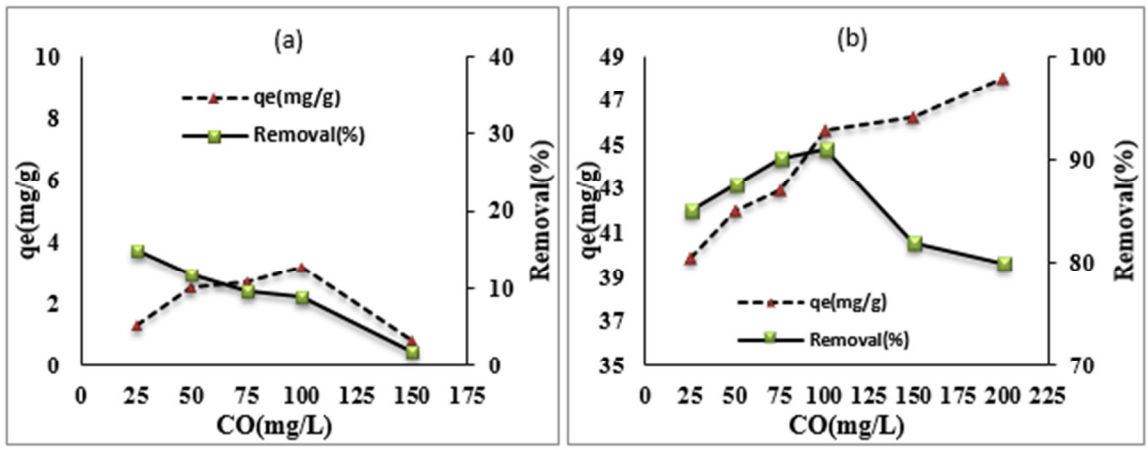

Figure 5: The effect of MB initial concentration on removal efficiency using: a) raw oak fruit hulls (contact time=360 min, pH=4, adsorbent concentration= 2g/L, MB, temperature=25 °C) and b) activated carbon (contact time=180, pH=6, adsorbent concentration= 2g/L, temperature=25 °C).

It was also observed that the dye adsorption capacity increases by dye concentration. The reason for the increase in dye adsorption capacity at higher concentrations can be explained as follows: By increasing the initial concentration of the force, the driving force toof the mass transfer also increases and the reaction between MB and adsorbent also increases. As a result, the absorption capacity also increases [45,46].

3.5. Effect of adsorbent concentration on MB adsorption efficiency

The effect of adsorbent concentration (0.5-3 g/L) was studied and the results are represented in Figure 6. It is clear that MB removal efficiency increases by the adsorbent concentration from 0.5 to 3 g/L. The increasing of MB adsorption efficiency may be due to the increase of the number of adsorption sites at the adsorbent surface at higher adsorbent concentrations [47, 48]. The dye adsorption increased up to the adsorbent concentration of 2 g/L and 3 g/L for activated carbon and raw oak fruit hulls, respectively, and then it reached equilibrium. The saturation of empty spaces or the aggregation/agglomeration of the adsorbent particles with each other has been considered as the main reasons for this phenomenon [49]. The above mentioned concentrations were considered as the optimum concentrations.

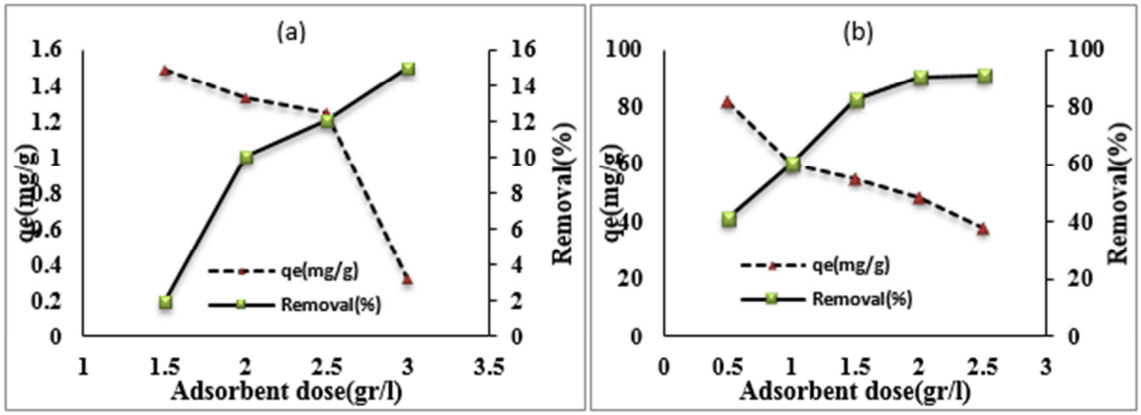

Figure 6: The effect of adsorbent concentration on MB removal efficiency using: a) raw oak fruit hulls (contact time=360 min, pH=4, initial MB concentration=25mg/L, MB, temperature=25°C) and b) activated carbon (contact time=180, pH=6, initial MB concentration=100 mg/L, temperature=25°C).

3.6. Isotherm studies

In adsorption of pollutants on various adsorbents, the determination of adsorption isotherm and adsorption capacity are the most important characteristics that should be considered. In order to study the isotherm of the MB adsorption, four models including Langmuir, Freundlich, Temkin and Dubinin-Radushkevich were utilized and the obtained results are represented in Table 3. Based on the previous studies, the Langmuir isotherm model is based on the monolayer and homogeneous adsorption of the adsorbate with the same energy on all surfaces of the adsorbent. In other words, it states that adsorption only occurs in certain and homogeneous sites without any reaction between the pollutant molecules and the absorbent, but the Freundlich isotherm is based on the multi-layered and heterogeneous adsorption of the adsorbate on the adsorbent. In addition, the Temkin model assumes that, due to adsorbate–adsorbent interactions, the heat of adsorption of all the molecules in a layer reduces linearly with surface coverage of adsorbent. Dubinin–Radushkevich isotherm is commonly used to articulate the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [50, 51]. Based on the results in Table 2, the best model to describe the MB adsorption onto the raw oak fruit hulls adsorbent and the activated carbon was the Langmuir model 1 (R^2=0.9971) and Langmuir model 2 (R^2=0.7631), respectively. Our results are consistent with the results of Gulnaz et al. [52].

3.7. Kinetic studies

Adsorption kinetics is important to understand the adsorption mechanisms and to assess the performance of adsorbents [53]. In this study, seven kinetic models were used for experimental data and for the prediction of absorption kinetics. The results are represented in Table 4. Based on the obtained results, the adsorption of MB onto the activated carbon are better fitted to pseudo-second-order model (R^2=0.9486). Moreover, the value q_{ecal} is close to $q_{e\ exp}$, which it also indicates the potential of this kinetic model to explain the equilibrium data. These results are consistent with the results of other studies [54-56]. In addition, the results of the studies on the raw oak fruit hulls adsorbent revealed that the adsorption of MB onto this adsorbent follows zero-order kinetic model, which there is no study consistent with observed results.

Table 3: The parameters calculated for isotherm models.

Models	Parameters	Oak fruit hulls adsorbent	Activated carbon prepared
Freundlich	N	0.68	0.36
	k_f	30.19	330
	R^2	0.5323	0.7692
Langmuir 1	q_m	0.33	57.8
	k_L	0.012	0.187
	R^2	0.3902	0.9971
Langmuir 2	q_m	50	6.96
	k_L	0.0014	0.07
	R^2	0.7631	0.9511
Langmuir 3	q_m	2.08	69.67
	k_L	0.04	0.174
	R^2	0.2173	0.605
Langmuir 4	q_m	80.4	80.4
	k_L	0.1	0.1
	R^2	0.2173	0.605
Temkin	q_m	1.65	10.757
	K_T	0.52	9.317
	R^2	0.4110	0.8343
Dubinin-Radushkevich	K_T	38.9	7943
	q_m	0.0001	0.000002
	R^2	0.7440	0.9685

Table 4: The parameters calculated for kinetic models.

Kinetic model	Parameter	Raw Oak fruit hulls adsorbent			Activated carbon prepared		
		Dye concentration (mg/L)			Dye concentration (mg/L)		
		25	50	100	50	100	200
Elovich	R^2	0.5357	0.6242	0.8037	0.9894	0.9770	0.9514
	β	1.72	1.93	2.5	28.31	30.60	22.47
	α	0.6	0.33	0.29	0.31	0.34	0.31
Zero order	q_{ecal}	0.2	1.011	0.377	20.47	17.2	6.22
	K_0	0.148-	-0.845	-0.751	-0.0173	-0.155	-0.268
	R^2	0.7996	0.988	0.9404	0.8645	0.9615	0.9682
First order	q_{ecal}	2.726	1.32	3.336	3.015	2.995	2.477
	K_1	-0.5374	-0.492	-0.9046	-0.0008	-0.0049	-0.009
	R^2	0.5396	0.7042	0.7444	0.875	0.981	0.9175

Table 4: Continue.

Kinetic model	Parameter	Raw Oak fruit hulls adsorbent			Activated carbon prepared		
		Dye concentration (mg/L)			Dye concentration (mg/L)		
		25	50	100	50	100	200
Second order	q_{ecal}	0.2	0.027	0.27	20.83	20.20	13.53
	K_2	-1.089	-5.944	-0.59	0.000003	0.0002	0.0004
	R^2	0.5882	0.1435	0.7452	0.8140	0.8704	0.7631
Pseudo-first order	q_{ecal}	3.93	89.1	67.6	2.47	56.69	117.37
	K_{1p}	-0.049	-0.2	-0.09	0.011	0.183	0.0215
	R^2	0.047	0.5350	0.73	0.4272	0.8014	0.8046
Pseudo-second order	q_{ecal}	0.21	0.66	0.1	23.92	58.13	149.25
	K_{2p}	-0.8	0.76	0.11	0.007	0.0002	0.00002
	R^2	0.083	0.2064	0.069	0.9999	0.9715	0.9486
Intraparticle diffusion	K_p	2.26	2.56	3.14	0.3636	2.976	5.137
	R^2	0.6033	0.7215	0.8295	0.9332	0.97	0.9825

4. Conclusion

In the present work, the ability of the studied adsorbent, i.e. raw oak fruit hulls and the activated carbon derived from it, in removing the Methylene Blue (MB) from aqueous solution was investigated. This study was conducted under various effective parameters including contact time, pH, MB concentration, adsorbent concentration and the optimum amount of each parameter were determined. Moreover, the isotherm and kinetic studies was carried out. The results revealed that the best results for MB removal efficiency are observed using the activated carbon derived from oak fruit hulls. It also observed that increasing the contact time, pH and adsorbent concentration provide better condition to enhance the dye removal efficiency and increasing the MB concentration is led to reduce the removal efficiency. Furthermore, the results also clarified that the best models to describe the MB adsorption onto the raw oak fruit hulls adsorbent and the activated carbon are the Langmuir model 1 and Langmuir 2, respectively. In addition, the adsorptions of MB onto the raw oak fruit hulls adsorbent and activated carbon are better fitted to pseudo-second-order model and zero-order model, respectively. It can be concluded that the activated carbon prepared from oak fruithull is better adsorbent to remove the MB.

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